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**APPLICATION NUMBER: 60/551,688**

**FILING DATE: *March 09, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/07938***



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030904 16711 U.S. PTO

22151 U.S. PTO  
60/551688

030904

DOCUMENT NUMBER

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CERTIFICATE UNDER 37 CFR 1.10:

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By: *Mary C. Netter*  
Name: Mary C. Netter

REQUEST FOR PROVISIONAL APPLICATION UNDER 37 C.F.R. § 1.53(c)

**MAIL STOP PROVISIONAL PATENT APPLICATION**

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Dear Sir:

This is a request for filing a Provisional application for patent under 37 CFR § 1.53(c) entitled REACTIVE OLIGOMERIC THIOL AND ENE MATERIALS AS DENTAL RESTORATIVE RESINS by the following inventor(s):

|                                    |  |  |  |
|------------------------------------|--|--|--|
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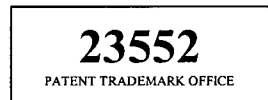
- ☒ Enclosed is the Provisional application for patent as follows: 33 pages of specification, and 0 sheets of drawings.
- ☐ Small entity status is claimed pursuant to 37 CFR 1.27.

The PTO did not receive the following listed item(s) 1 page of SPFC

3. ☒ Payment of Provisional filing fee under 37 C.F.R. § 1.16(k) :  
☒ Attached is a check in the amount of \$ 160.00.  
☐ Please charge Deposit Account No. 13-2725.  
☐ PAYMENT OF THE FILING FEE IS BEING DEFERRED.
4. ☒ The Commissioner is hereby authorized to charge any additional fees as set forth in 37 CFR §§ 1.16 to 1.18 which may be required by this paper or credit any overpayment to Account No. 13-2725.
5. ☐ Enclosed is an Assignment of the invention to \_\_\_\_\_, Recordation Form Cover Sheet and a check for \$ \_\_\_\_\_ to cover the Recordation Fee.
6. ☐ Also Enclosed:
7. ☒ The invention was made by the following agency of the United States Government or under a contract with the following agency of the United States Government: NIH Research Grant #DE10959.
8. ☒ Address all future communications to the **Attention of George C. Lewis** (may only be completed by attorney or agent of record) at the address below.
9. ☒ A return postcard is enclosed.


Respectfully submitted,

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Date:

3/9/04

  
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GCLewis:mcn

## **Invention Title.**

Reactive Oligomeric Thiol and Ene Materials as Dental Restorative Resins

## **Abstract**

Dimethacrylate photopolymerizable polymer composites have been a leading choice for dental restorations for over thirty years. However, volume shrinkage and shrinkage induced stress, a result of the double bond conversion, often lead to premature failure of the restoration. An innovative approach to low shrinkage dental resin through the utilization of thiol-ene systems has recently been proposed. This invention develops thiol-ene materials as dental restorative resins through the novel approach of prepolymerization (oligomerization) of thiol and ene monomers to form oligomeric thiol and ene material to be used as ultra-low shrinkage and ultra-low shrinkage stress dental material. The resultant volume shrinkage for oligomeric thiol-enes is 50% less than monomeric thiol-enes and 75% less than standard dimethacrylate systems.

## **Background**

Currently, commercial photoactivated dental restorative resins are based on dimethacrylates and the reaction mechanism is through chain-growth free radical polymerization. Existing dimethacrylate systems are popular for fillings and other dental prostheses because of their esthetic merit and "cure-on-command" feature.

Such dental restorative materials are often mixed with 45 to 85 wt% silanized filler compounds such as barium, strontium, zirconia silicate and/or amorphous silica to match the color and opacity to a particular use or tooth. The filler is typically in the form of particles with a size ranging from 0.01 to 5.0micrometers.

The photoactivated restorative materials are often sold in separate syringes or single-dose capsules of different shades. If provided in a syringe, the user dispenses (by pressing a plunger or turning a screw adapted plunger on the syringe) the necessary amount of restorative material from the syringe onto a suitable mixing surface. Then the material placed directly into the cavity, mold, or location of use. If provided as a single-dose capsule, the capsule is placed into a dispensing device that can dispense the material directly into the cavity, mold, etc. After the restorative material is placed, it is photopolymerized or cured by exposing the restorative material to the appropriate light source. The resulting cured polymer may then be finished or polished as necessary with appropriate tools. Such dental restoratives can be used for direct anterior and posterior restorations, core build-ups, splinting and indirect restorations including inlays, onlays and veneers.

Although easy to use, these systems have several drawbacks, primarily associated with the polymerization volume shrinkage and shrinkage stress, and poor conversion of the dimethacrylate systems' monomers into polymer. The current systems can only reach a final double bond conversion of 55 to 75 %, which not only contribute to the insufficient wear resistance and mechanical properties, but also jeopardizes the biocompatibility of the composites due to the leachable unreacted monomers. Dimethacrylate based resins exhibit significant volumetric shrinkage during polymerization and the induced shrinkage stress results in tooth-composite adhesive failure, initiating microleakage and recurrent caries, which significantly reduces the longevity and utility of current dental restorative composite. Furthermore, as one tries to increase the final double bond conversion to reduce the unreacted monomers, the volumetric shrinkage and shrinkage stress unfortunately also increase, which has been a persisting problem since the development of this class of resins.

## **Description of the Invention**

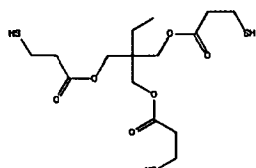
The present invention can be thought of as a thiol-ene system with a high conversion, low shrinkage and low odor during curing. A thiol-ene system having 15%-60% by weight of its functional groups as thiol functional groups is disclosed. The balance of the functional groups in the system can be vinyl groups. The vinyl groups may be provided by vinyl ethers, acrylates or other monomers containing vinyl groups. In addition to thiols and vinyl groups, additional functional groups may be provided to tailor and provide additional properties.

Thiol-ene systems may also include and/or utilize various initiators, fillers, and accelerators depending on the application. For example, if photopolymerization using visible light is desired, camphorquinone may be used as an initiator. Alternatively, if ultraviolet photopolymerization is desired, then 2,2-dimethoxy-2-phenylacetophenone (DMPA) may be used as an initiator. Amine accelerators may also be used, as well as other accelerators. However, we have found that thiol-ene system can be readily initiated by just camphorquinone, without the presence of the amine accelerator. This is largely beneficial to the biocompatibility of photo-cured dental composites since studies have shown that certain tertiary amine accelerators, such as N,N-dimethyl-p-toluidine, are carcinogenic and mutagenic.

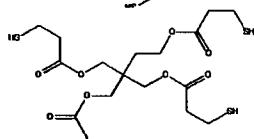
The thiol-ene systems of the present invention have some significant and unique advantages compared with (meth)acrylate polymerizations, which are extremely beneficial for dental resin applications. These advantages include: high gel-point conversion which will significantly decrease shrinkage stress; rapid polymerization rate and lack of oxygen inhibition; nearly complete consumption of low molecular weight reacting species due to the nature of the step-growth mechanism, which limits the amount of leachable species and exhibiting less perceptible odor; versatile kinetics and structure-property design based on tailoring the thiol-ene monomer chemistry.

Another advantage of thiol-ene systems is that they can replace existing methacrylate systems. Thiol-ene polymers can be mixed and applied in the same manner currently used by dentists using methacrylate systems. The thiol-ene systems can be mixed with fillers as is typical in methacrylate systems. Depending on the initiator used, existing light sources used to photopolymerize the methacrylate systems may also be used. Likewise, dental restorative materials using thiol-ene polymer systems may be supplied in single-dose capsules or syringes.

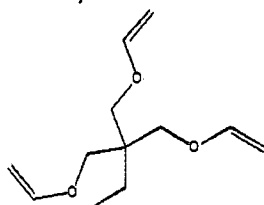
Our work on oligomeric thiol and ene material as dental restorative material has focused on the creation and purification of oligomeric thiol and ene material from commercially available monomers, and demonstrating the advantages of these oligomeric polymers over current dental restorative materials. The specific monomers used are depicted below:



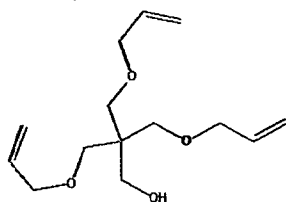
Trimethylolpropane tris(3-mercaptopropionate) (**Trithiol**)



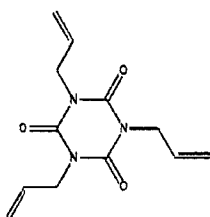
Pentaerythritol tetrakis(3-mercaptopropionate) (**Tetrathiol**)



Trimethylolpropane trivinyl ether (**Trivinyl**)

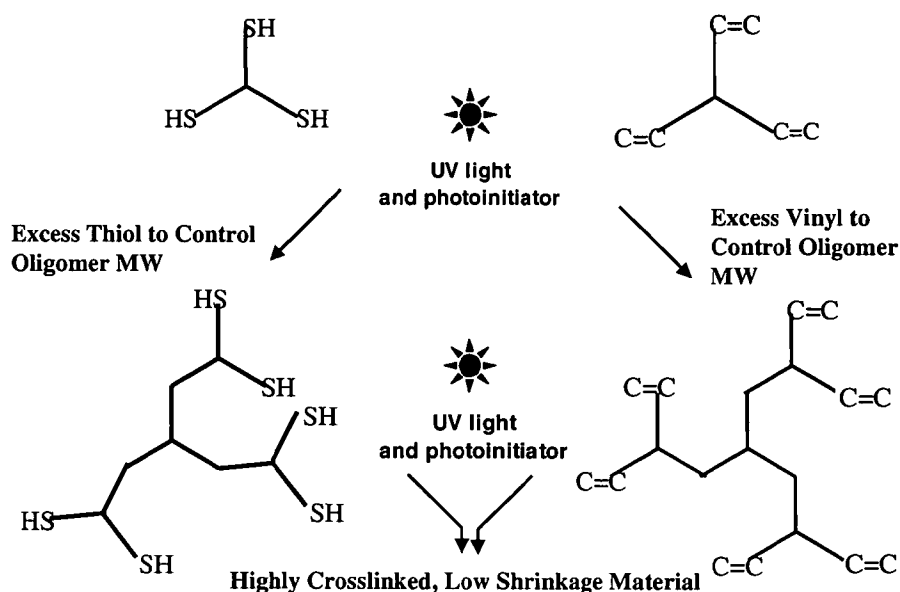


Pentaerythritol triallyl ether (**Triallyl**)



1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (**Triazine Triallyl**)

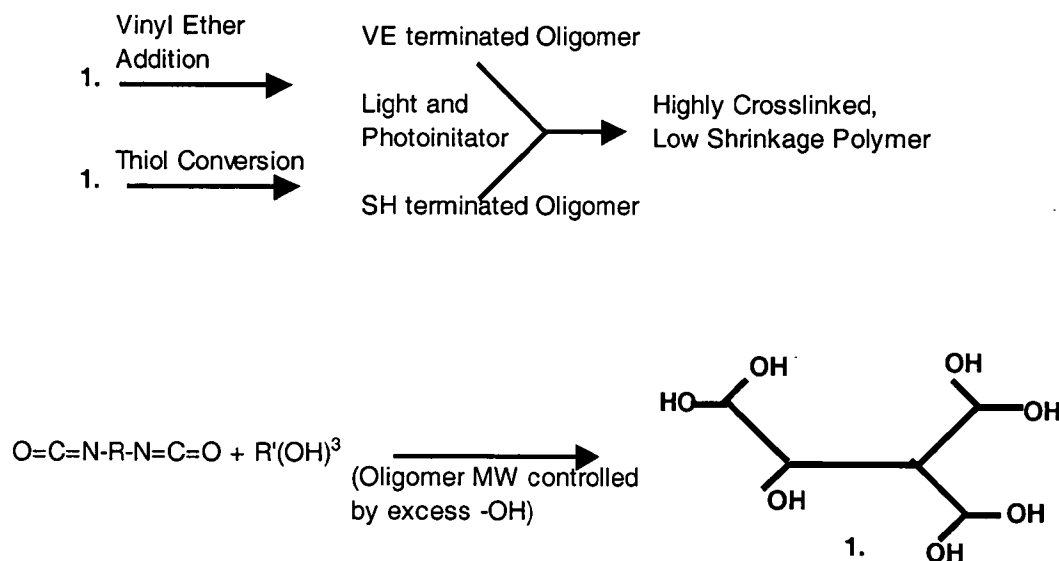
**Photopolymerization to form reactive, oligomeric thiol and ene material.** One unique advantage of the step growth mechanism is that it affords greater control over the molecular weight, molecular weight distribution, and terminal functionality than does a traditional free radical photopolymerization. By performing the photopolymerization (outside the cavity or body well before the material is needed) with an excess of either the vinyl or thiol functionality, it is possible to form highly functional, reactive oligomers that are nearly exclusively one functional group terminated. This concept is shown in Figure 1. Once the thiol and vinyl functionalized oligomers have been synthesized and purified, they can be mixed stoichiometrically and reacted to form a highly crosslinked polymer network with properties that are nearly identical to those of the system that would be formed from the bulk stoichiometric monomer polymerization.



**Figure 1. Oligomerization photopolymerization scheme.**

**Isocyanate –Alcohol reactions to form reactive oligomers.** This process appears much like the first process; however, here the functional groups (i.e. the alcohol and isocyanate) will react in a true stepwise manner as through a typical condensation reaction. An excess amount of alcohol fed to the reacting system will prevent gelation and lead to, at 100% conversion of the isocyanates, a highly functional system with all alcohol functional groups at the ends. The alcohols will subsequently be converted either to vinyl ethers (or other vinyls) or to thiols by synthetic means, via mechanism documented elsewhere<sup>1,2</sup>. In either case, a large fraction of the reaction (and therefore shrinkage) will occur outside of the actual filling, lowering the shrinkage and the polymerization exotherm. Two reasons exist for pursuing this strategy. The first involves enhanced chemical flexibility. The availability of thiols and vinyl containing compounds is limited. Thus, this second strategy allows us to begin the oligomerization process with a greater variety of chemical structures available. Secondly, the same oligomeric products can be derivatized with both vinyl and thiol functional groups (in two separate batches) to facilitate miscibility that might not otherwise be possible. A schematic of this overall process is presented in the Figure 2 for a diisocyanate and a triol (in excess). This approach can be readily adapted to a variety of coupling chemistries.





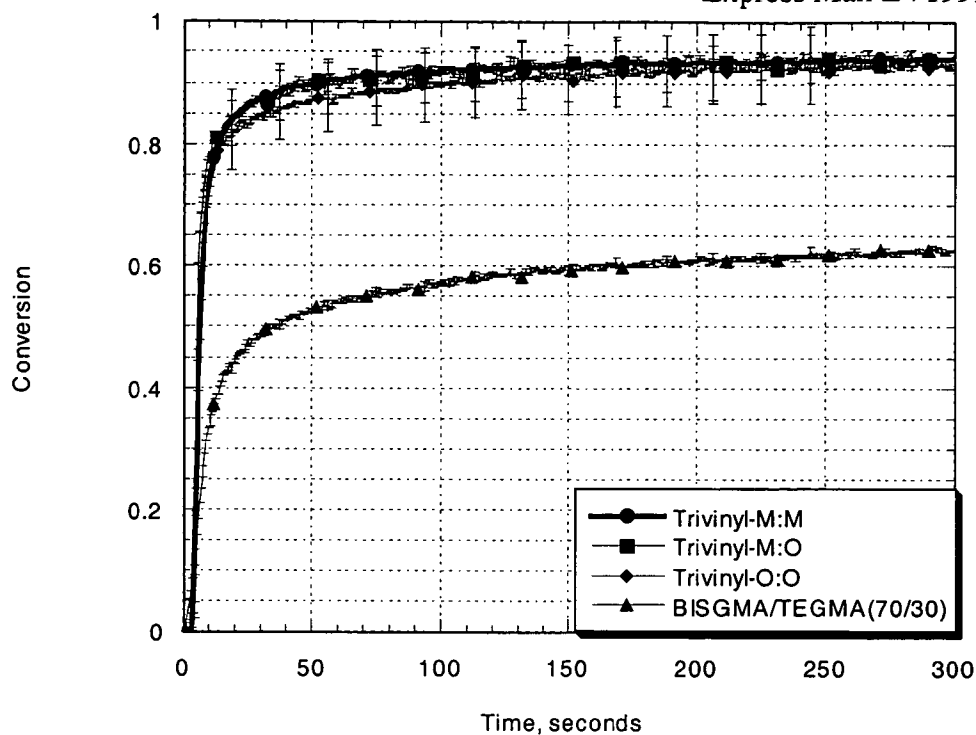
**Figure 2. Isocyanate –Alcohol oligomerization scheme.**

1. Okimoto, et al. (2002). Development of a highly efficient catalytic method for synthesis of vinyl ethers. J. Am. Chem. Soc., 124:1590-1591.
2. Krishnamurthy, S. and Aimino, D. (1989). Journal of Organic Chemistry 54(18):4458-4462.

Both of which references are herein incorporated by reference.

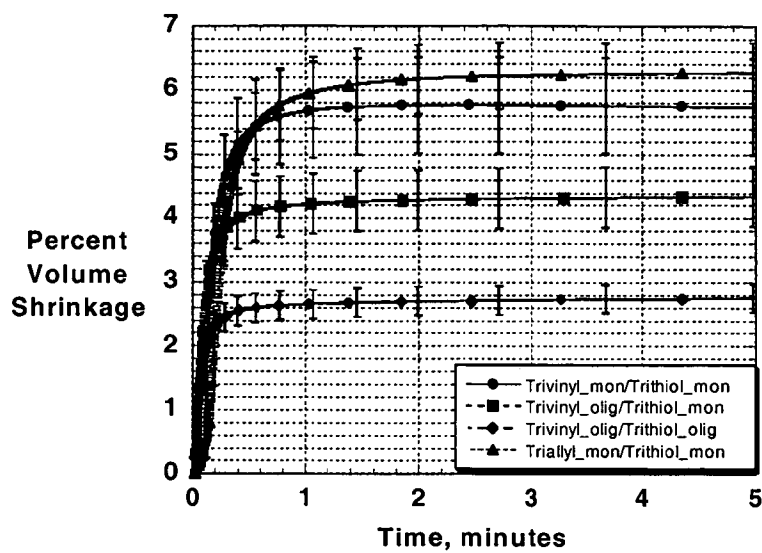
#### **Polymerization kinetics investigation of oligomeric thiol and ene systems.**

FTIR (Magna 750, Nicolet Instrument Corp., Madison WI) was used to study the polymerization kinetics of the oligomeric thiol-ene materials used in this study because of its inherent advantage of being able to measure the thiol and vinyl conversions simultaneously and rapidly. The infrared peak at  $1643 \text{ cm}^{-1}$  was used to determine the vinyl conversion, and the peak at  $2572 \text{ cm}^{-1}$  was used for the thiol group conversion. As shown in Figure 3, the final conversion of the vinyl for the Trithiol/Trivinyl system was found to be  $93.8\% \pm 0.8\%$ , where as the BisGMA/TEGDMA (70/30) reached a final conversion of only  $65\% \pm 0.8\%$ . Furthermore, the final conversion for the vinyl functional group in the trithiol/trivinyl oligomer (M:O) and trithiol oligomer/trivinyl oligomer(O:O) is statistically indistinguishable from the conversion of trithiol/trivinyl(M:M), showing that prepolymerization of the monomers does not effect the final conversion or mechanical properties of the polymer. Furthermore, the polymerization for monomeric and oligomeric systems occurs at a much higher rate and achieves a higher final conversion than the bis-GMA/TEGDMA (70/30 by wt.) when cured under the same conditions.

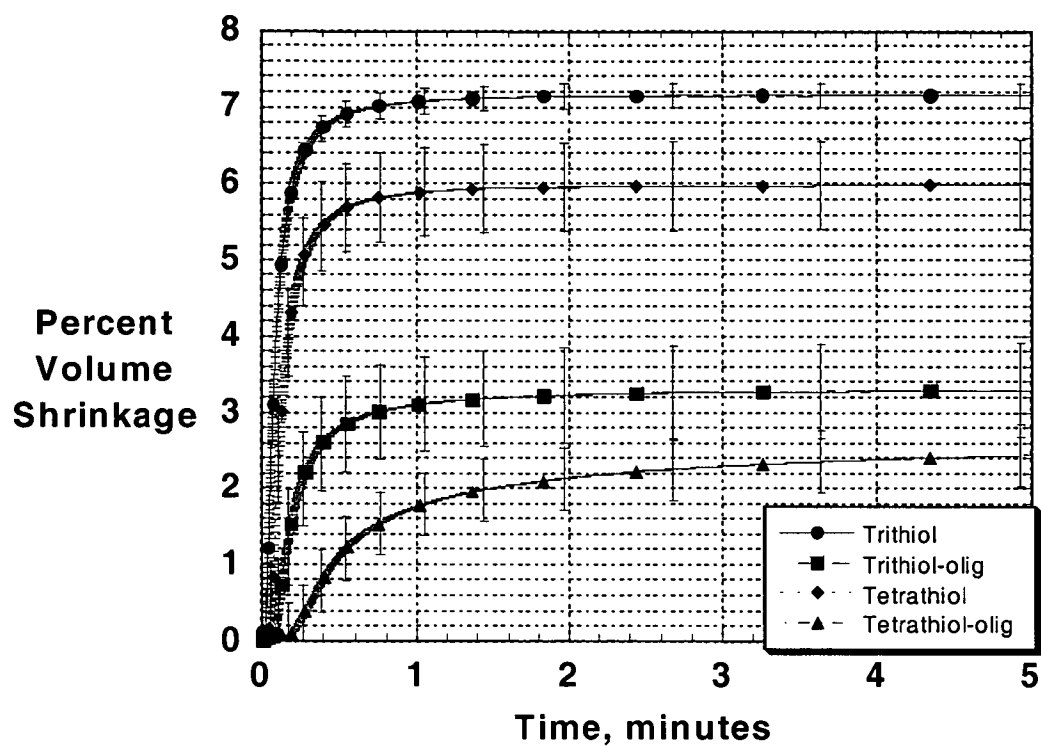


**Figure 3.** Conversion of the vinyl functional group for Trithiol/Trivinyl (M:M), Trithiol/Trivinyl Oligomer (M:O), Trithiol oligomer/Trivinyl oligomer (O:O), and Bis-GMA/TEGDMA (70/30 by wt.) as a function of irradiation time; 0.1 wt% DMPA; UV=15mW/cm<sup>2</sup>. The thiol-ene monomer mixture was prepared to have an equivalent concentration of the two functional groups.

**Polymerization shrinkage investigation of oligomeric thiol and ene systems.** An ACTA linometer (Academic Center for Dentistry Amsterdam, Department of Dental Materials Science, Amsterdam, The Netherlands) was used to measure the post-gel linear polymerization shrinkage of oligomeric resins. All systems were cured as bulk solutions (no dental filler). As seen in Figures 4, the Trithiol/Trivinyl achieves percent volume shrinkage of 5.7% +/- 0.8%, and the Trithiol/Triallyl resin achieves a volume shrinkage of 6.5% +/- 0.6%. This is significantly less shrinkage than the shrinkage of Bis-GMA/TEGDMA (70/30 by wt.) at the same conversion (Table 1 depicts theoretical shrinkage for Bis-GMA/TEGDMA and thiol-ene systems). Oligomerization of the trivinyl lowers the shrinkage to 4.4% +/- 0.5% and oligomerization of the Trivinyl and the Trithiol lowers the shrinkage to 2.5% +/- 0.5%, which are statistically ( $\alpha=0.05$ ) significant decreases in volume shrinkage, while maintaining the final conversion. Figure 5 depicts similar trends using the Triazine Triallyl monomer with Trithiol and Tetrathiol and their respective oligomers.



**Figure4.** Percent volume shrinkage for Trithiol/Triallyl, Trithiol/Triviny, Trithiol/Triviny oligomer, and Trithiol oligomer/Triviny oligomer systems as a function of time; 0.1wt% DMPA, UV=15 mW/cm<sup>2</sup>. All mixtures were prepared to have an equivalent concentration of the two functional groups.



**Figure5.** Percent volume shrinkage for Trithiol/Triazine Triallyl, Trithiol oligomer/Triazine Triallyl, Tetrathiol/Triazine Triallyl, and Tetrathiol oligomer/Triazine Triallyl systems as a function of time; 0.1wt% DMPA, UV=15 mW/cm<sup>2</sup>. All mixtures were prepared to have an equivalent concentration of the two functional groups.

### Simultaneous measurement of thiol-ene shrinkage stress and conversion

Using a tensometer designed by the American Dental Association, shrinkage stress was measured as a function of conversion. As seen in Figure 6, the final shrinkage stress achieved by Trithiol/Triazine Triallyl was 0.86  $\pm$  0.08 MPa, whereas the final shrinkage stress achieved by Trithiol Oligomer / Triazine Triallyl was 0.31  $\pm$  0.08 MPa. This extremely low shrinkage stress of the oligomeric system is a result of the reduced concentration of vinyl groups in the final mixture.

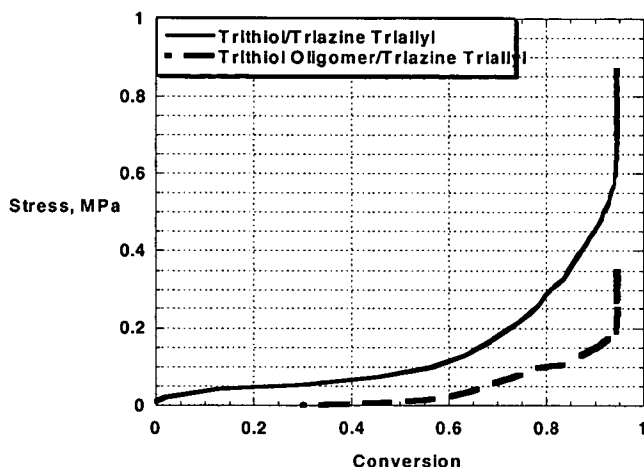


Figure 6. Shrinkage stress as a function of double bond conversion of Trithiol and Trithiol oligomer reacted with Triazine Triallyl, cured with UV=17mW/cm<sup>2</sup> for 50 seconds at room temperature.

| SYSTEM                       | % thiol<br>conversion | theoretical<br>% vol.<br>Shrinkage |
|------------------------------|-----------------------|------------------------------------|
| Bis-GMA/TEGDMA (70/30)       | 65                    | 9.2                                |
| Bis-GMA/TEGDMA (70/30)       | 100                   | 12.2                               |
| triazine triallyl / trithiol | 96                    | 7.8                                |
| triallyl / trithiol          | 98                    | 6.3                                |
| trivinyl / trithiol          | 94                    | 7.8                                |

**Table 1.** Theoretical percent Volume Shrinkage for bis-GMA/TEGDMA and thiol-ene (equivalent concentration of functional groups) systems.

Current polymerizable dental resins consist of dimethacrylate monomers. While the dimethacrylate resin has decent mechanical properties for dental material use, it does exhibit polymerization shrinkage, shrinkage induced stress, water uptake which leads to microcracks and loss of adhesion, ultimately leading to premature failure of the resin <sup>3,4</sup>. Recently, the primary inventor has proposed thiol-ene resins as dental materials since they offer improved control of polymerization and delayed gel point as a result of their step-growth polymerization (versus the chain growth mechanism of the current dimethacrylate system). In addition, thiol-ene resins demonstrate a dramatic reduction in shrinkage, a lack of oxygen inhibition and the possibility of a photoinitiator free system <sup>5</sup>. Building on the advantages of the step-growth mechanism, it is possible to oligomerize thiol and ene monomers, achieving a higher extent of polymerization prior to formulating the final resin and completing the polymerization in the restoration. This will decrease the functional group concentration, more specifically the vinyl functional group concentration, which is responsible for shrinkage, thus creating an even lower shrinkage material than the dimethacrylate and monomeric thiol-ene systems, while maintaining mechanical integrity. Furthermore, oligomerization of thiol and ene materials eliminates low molecular weight reactants responsible for odor, as well as reduces the amount of extractable monomer in the resin, reducing the cytotoxicity of the resin. Oligomerization of thiol and ene material for optical fiber coating has been demonstrated in U.S. patent 5,459,175.

3. Craig, R.G., O'Brien, W., and Power, J. (1996) *Dental Materials: Properties and Manipulation*. Mosby, St. Louis.

4. Craig, R.G., editor (1997). *Restorative Dental Materials*. Mosby, St. Louis, 10<sup>th</sup> edition.

5. Cramer, N.B., and Bowman, C.N. (2001). Investigation into the Kinetics of thiol-ene and Thiol-acrylate photopolymerizations using real-time FTIR. *Journal of Polymer Science, Part A: Polymer Chemistry*, 39:3311-3319.

Current dental resins react via a chain growth mechanism, whereas the proposed thiol-ene systems react via a step growth mechanism, which allows for the novel oligomerization of thiol and ene materials. Furthermore, oligomerization is possible to accomplish outside of the cavity before the material is needed.

Oligomeric thiol and ene polymers will dramatically increase the lifespan of dental restorative composites because of the ultra-low shrinkage exhibited by these materials. Companies that manufacture dental restorative composites will find oligomeric thiol and ene materials novel and beneficial to their formulations. The incorporation of oligomeric thiol and ene materials into dental composites will benefit the millions of patients who require dental procedures. Hence, this invention will be of importance in the dental and biomedical community.

## IV. SPONSORSHIP

### A. Government Agency Contract / Grant No. / Title / PI.

NIH Research Grant #DE10959

## Claims

What is claimed is:

1. A method comprising:

polymerizing vinyl monomers having vinyl functional groups in an excess of thiol monomers having thiol functional groups to obtain first oligomers having thiol functional groups;  
polymerizing thiol monomers having thiol functional groups in an excess of vinyl monomers having vinyl functional groups to obtain second oligomers having vinyl functional groups;  
stoichiometrically mixing the first oligomers and the second oligomers to obtain a first mixture.

2. The method of claim 1 further comprising:

polymerizing the first mixture.

3. The method of claim 1 further comprising:

mixing the first mixture with a filler having a color and a photoinitiator to obtain a second mixture.

4. The method of claim 3 further comprising:

packaging the second mixture in a container based on the color of the filler.

5. The method of claim 4 further comprising:

dispensing the second mixture;  
shaping the second mixture into a dental prosthesis; and  
photopolymerizing the second mixture.

6. The method of claim 1 further comprising:

reacting an isocyanate ( $\text{O}=\text{C}=\text{N}=\text{R}=\text{N}=\text{C}=\text{O}$ ) in an excess of alcohol ( $\text{X}-\text{OH}$ ) to form alcohol monomers having alcohol functional groups;  
reacting alcohol monomers with vinyl ethers to form the vinyl monomers; and  
reacting alcohol monomers with thiols to form the thiol monomers.

## APPENDIX A –

Presentation on Reactive Oligomeric Thiol and Ene Materials as Dental Restorative Resins

To be given on March 12, 2004.



# Reactive Oligomeric Thiol and Ene Materials as Dental Restorative Resins

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Jacquelyn Carioscia

IADR

March 12, 2004

# Project Objective

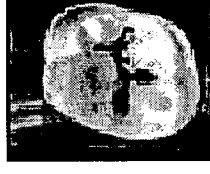
Improve the mechanical response and longevity of polymeric dental resin through the implementation of a thiol-ene photopolymerizable matrix.

- Factors of thiol-ene polymer mechanical properties
  - monomer backbone chemistry
  - monomer functionality
  - reaction state (monomer vs. prepolymer)
- Experimental analysis protocol
  - FTIR analysis
  - DMA analysis
  - Linometer analysis

# Dental Restoration History

- **Amalgam**

- Good mechanical properties and longevity of restoration
- Requires mechanical undercuts
- Toxicological issues



- **Polymer Resin: Bis-GMA/TEGDMA**

- Aesthetic appeal
- Less invasive procedure
- Polymerization volume shrinkage and shrinkage induced stress
- Low wear resistance, swelling, lack of color longevity
- Incomplete conversion → leachable monomer
- Initiator sensitization
- High coefficient of thermal expansion



**Novel Solution: Thiol-ene resin**

# Thiol-Ene Polymerization Mechanism



## ● Advantages

- ✓ Improved control of polymerization
- ✓ Delayed gel point
- ✓ Higher consumption of low molecular weight species
- ✓ Lack of oxygen inhibition
- ✓ Possibility of photoinitiatorless system
- ✓ More homogeneous network

# Reactive Oligomeric Thiol and Ene Material

- **Why create reactive oligomers?**
  - Limits reactive C=C bonds in mixture
  - Eliminate olfactory offensive thiols

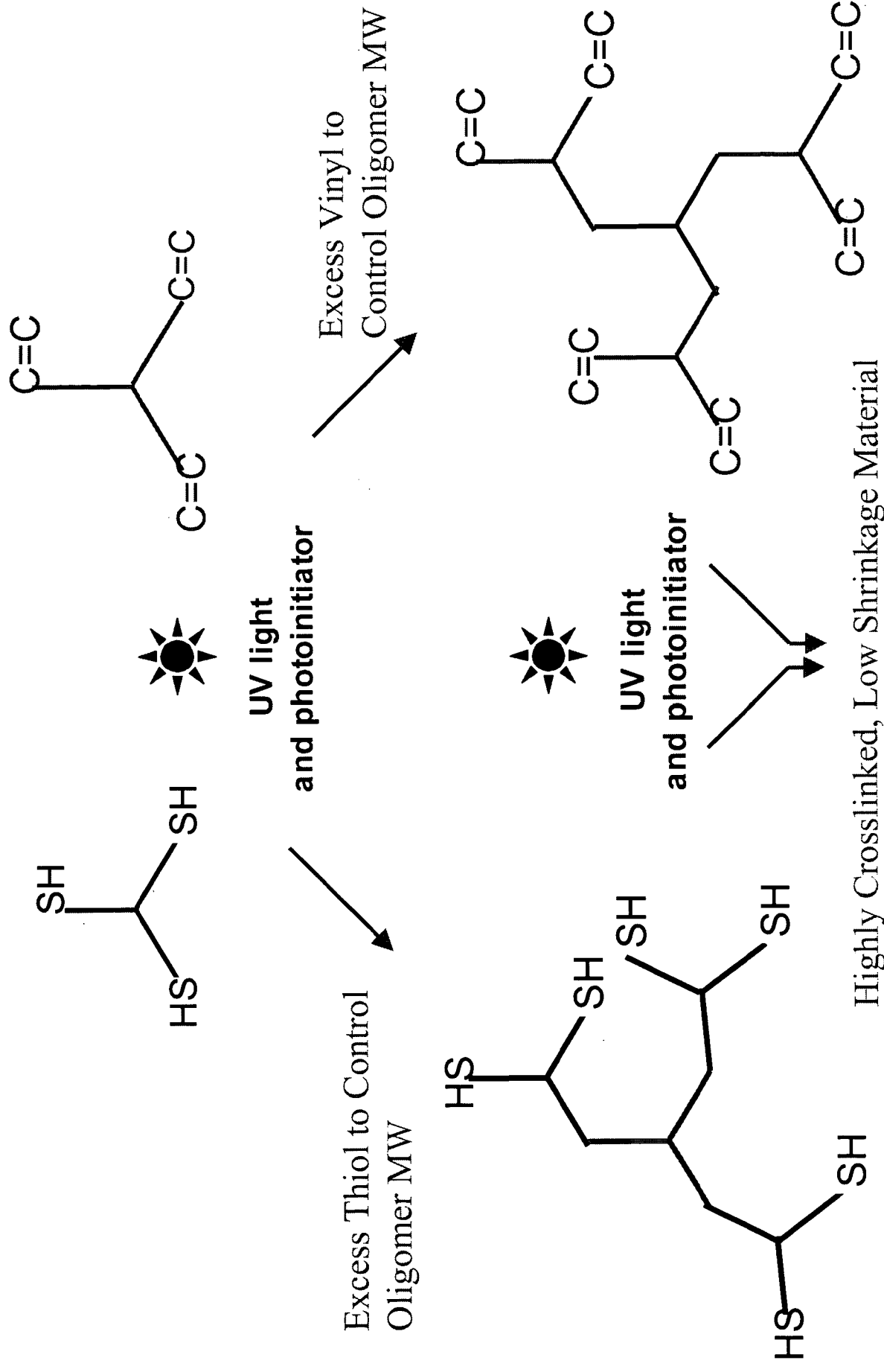
The step growth polymerization gelation equation is given by:

$$r = \frac{1}{\alpha^2 (f_a - 1)(f_b - 1)}$$

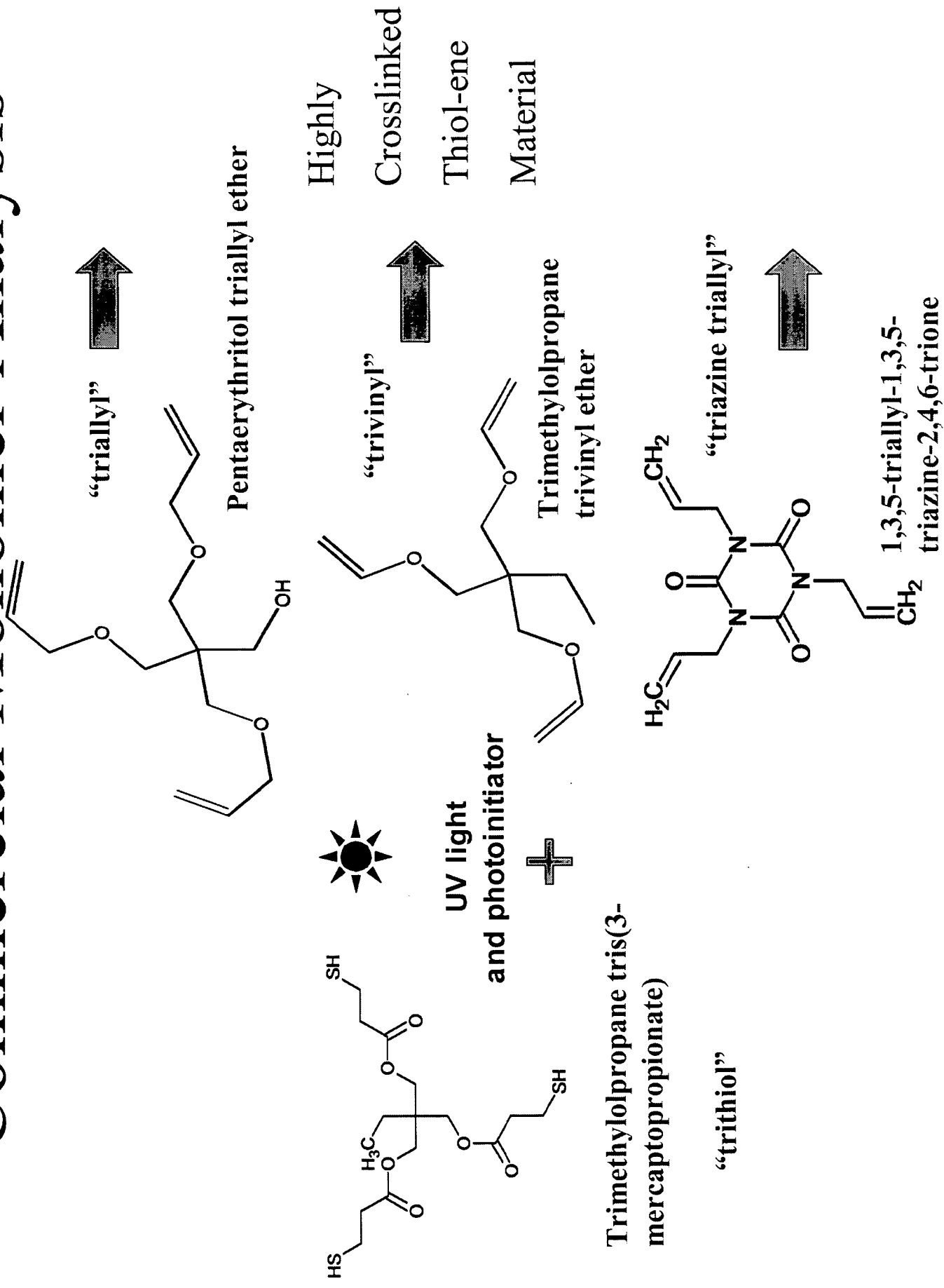
where **alpha** is the fractional conversion required for gelation, **fa**, **fb** are monomer functionalities, and **r** is the stoichiometric monomer functionality ratio

- ✓ Non-gelled oligomers are formed when alpha is larger than one
- ✓ By manipulating the gelation equation, **r** can be determined to create oligomer with the desired functionality

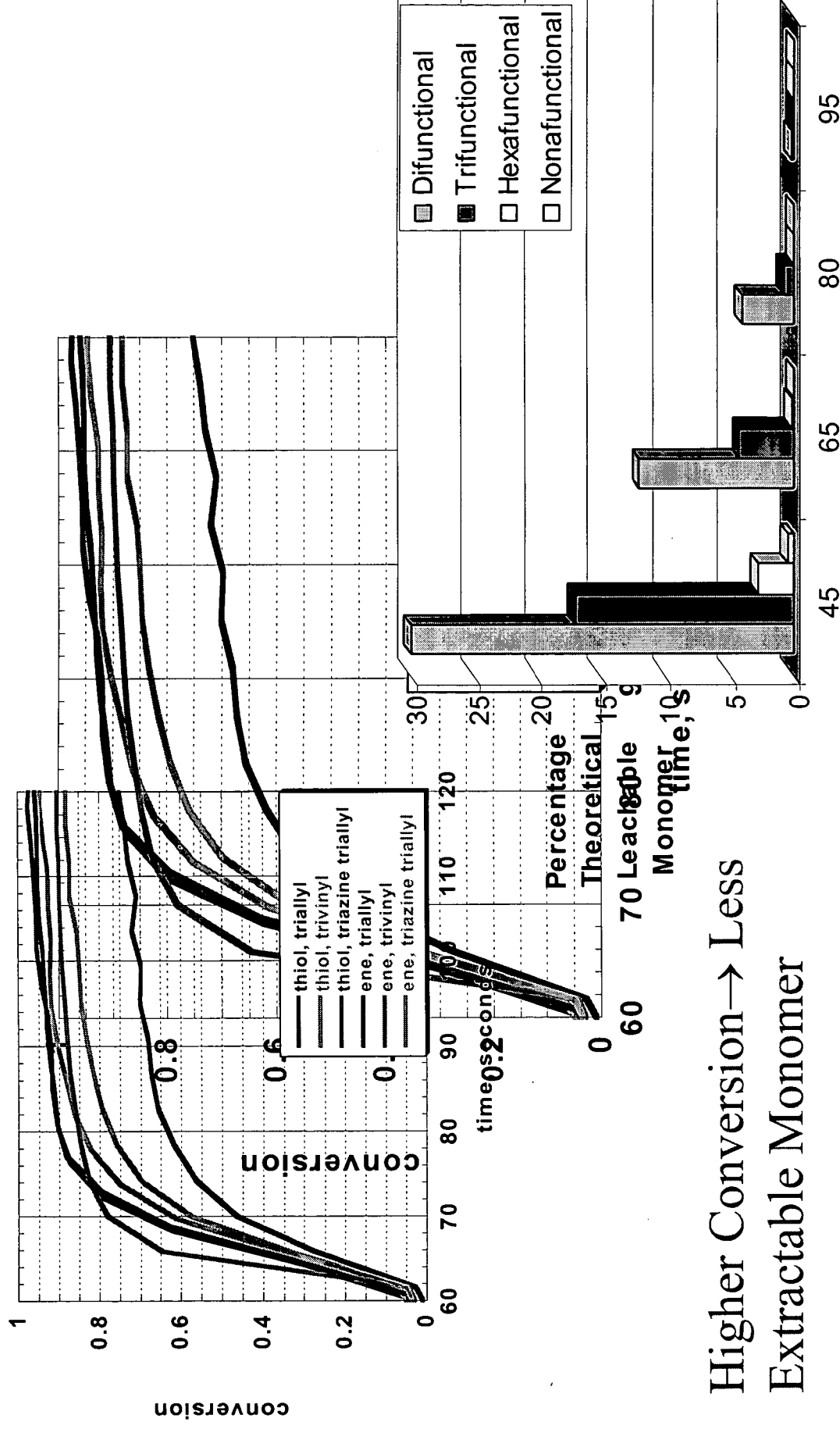
# Prepolymerization: Forming Reactive Oligomers



# Commercial Monomer Analysis



# Conversion Results



Higher Conversion → Less Extractable Monomer

Polymerized at 15mW/cm<sup>2</sup> for 400seconds, 0.1wt% DMPA

Thiol standard deviation ranges from  $\pm 1.4\%$  to  $\pm 2.7\%$ , and ene standard deviation ranges from  $\pm 0.8\%$  to  $\pm 2.9\%$  ( $n=4$ ).



# Volume Shrinkage

- **Why is polymerization shrinkage important?**

As little as 2% volume shrinkage can cause premature failure.

- Reaction of vinyl group causes shrinkage

- ✓ Thiol-ene Shrinkage: 12-15 ml/mol C=C mole polymerized§
- ✓ Methacrylate system shrinkage: 22.5 ml/mole C=C polymerized\*

- Bis-GMA/TEGDMA volume shrinkage

- ✓ 8%, unfilled †
- ✓ 1.56-3.4%, filled‡

| SYSTEM                       | % vinyl conversion | theoretical % vol. Shrinkage |
|------------------------------|--------------------|------------------------------|
| Bis-GMA                      | 41                 | 4.2                          |
| Bis-GMA                      | 95                 | 9.6                          |
| Bis-GMA/TEGDMA (50:50)       | 67                 | 9.2                          |
| triazine triallyl / trithiol | 96                 | 7.8                          |
| triallyl / trithiol          | 98                 | 6.3                          |
| trivinyl / trithiol          | 94                 | 7.8                          |

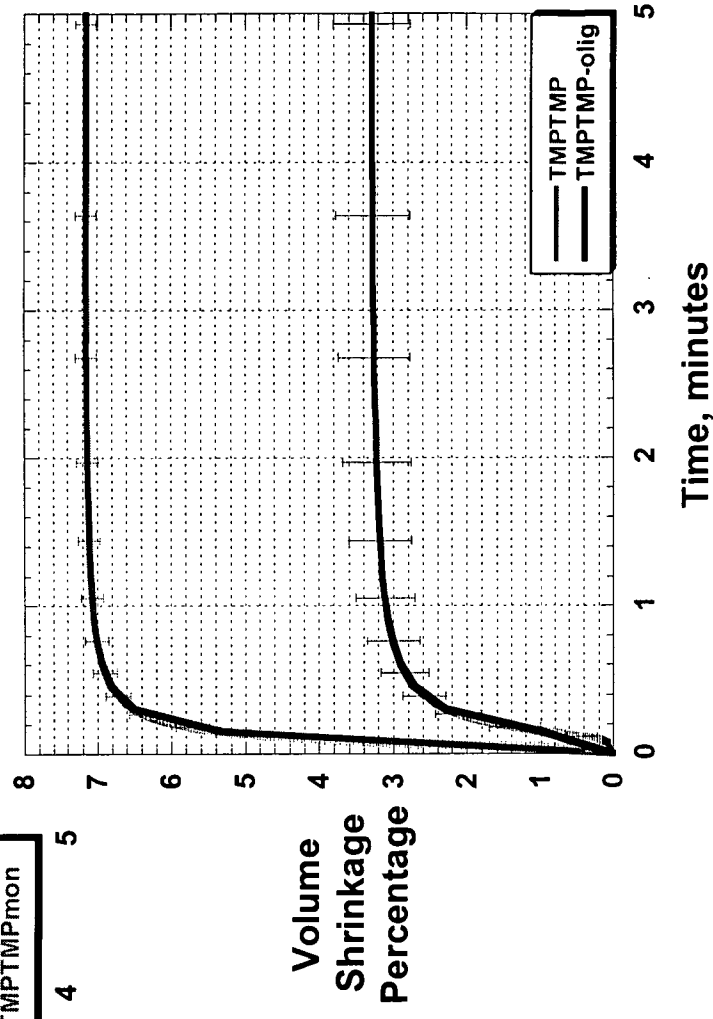
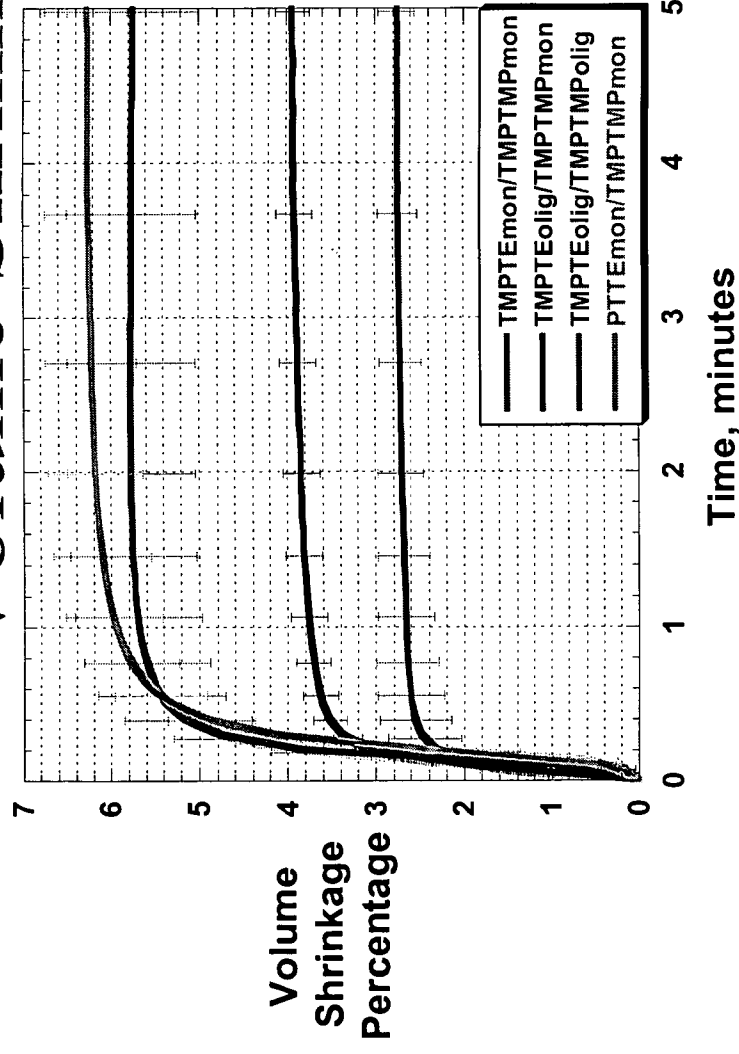
§Lu, H. Bowman, C. University of Colorado, Boulder, CO. Unpublished work, 2002..

\*Patel, M.P., Braden, M., and Davy, K. W.M. Biomaterials, **8**,53-56, (1987).

† Khatri, C., Stansbury, J., Schutheisz, C., and Antonucci, J. Dental Materials **19** ,584-588, (2003).

‡ Iga, M., Takeshige, F., Ui, T., and Torii, M. Dental Materials Journal **10** (1), 38-45, 1991.

# Volume Shrinkage Results



- ✓ Homopolymerizable monomers exhibit more shrinkage than non-homopolymerizable
- ✓ Prepolymerizing significantly reduces polymerization shrinkage

0.1 wt% DMPA, 15 mW/cm<sup>2</sup>, 400 second cure

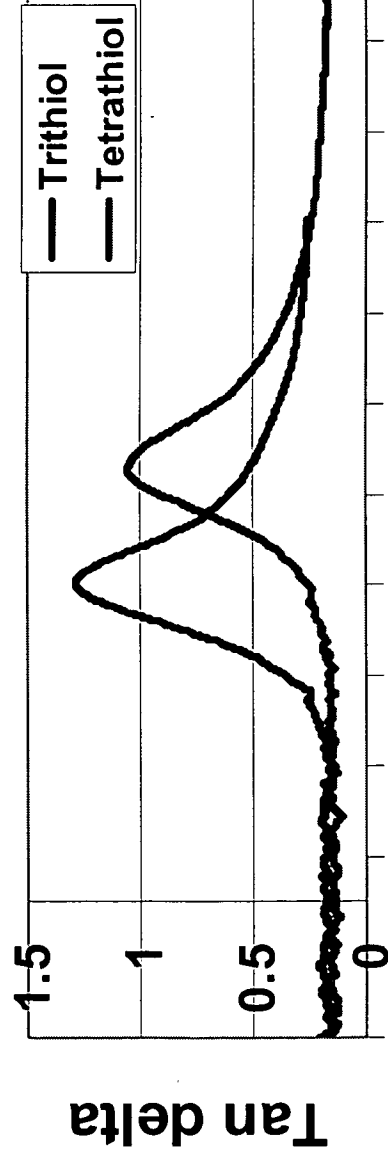
# Glass Transition Temperature

- **Why is the glass transition temperature important?**
  - ✓ Determines restoration operating temperature
  - ✓ Evaluates resin homogeneity

| THIOL    | ENE                     | T <sub>g</sub> (°C) |
|----------|-------------------------|---------------------|
| Trithiol | Trivinyl                | 1.7 ± 0.1           |
| Trithiol | Triallyl                | -2.2 ± 1.3          |
| Trithiol | Triazine Triallyl       | 33.8 ± 1.3          |
| na       | bisGMA/TEGDMA , 75%/25% | 52.4 ± 0.6          |

DMA scan over temperature range -50-150 °C with a ramping rate of 5 °C per minute using extension mode. Specimen UV cured at room temp.(15mW/cm<sub>2</sub>, 0.1wt%DMPA). Standard deviation is ±1.3 degrees (n=3).

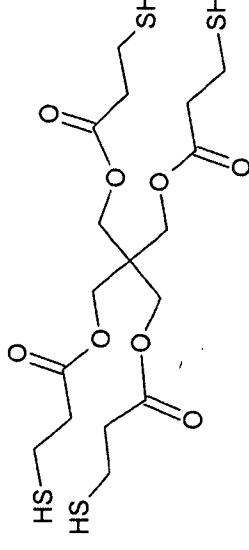
# Tg Results



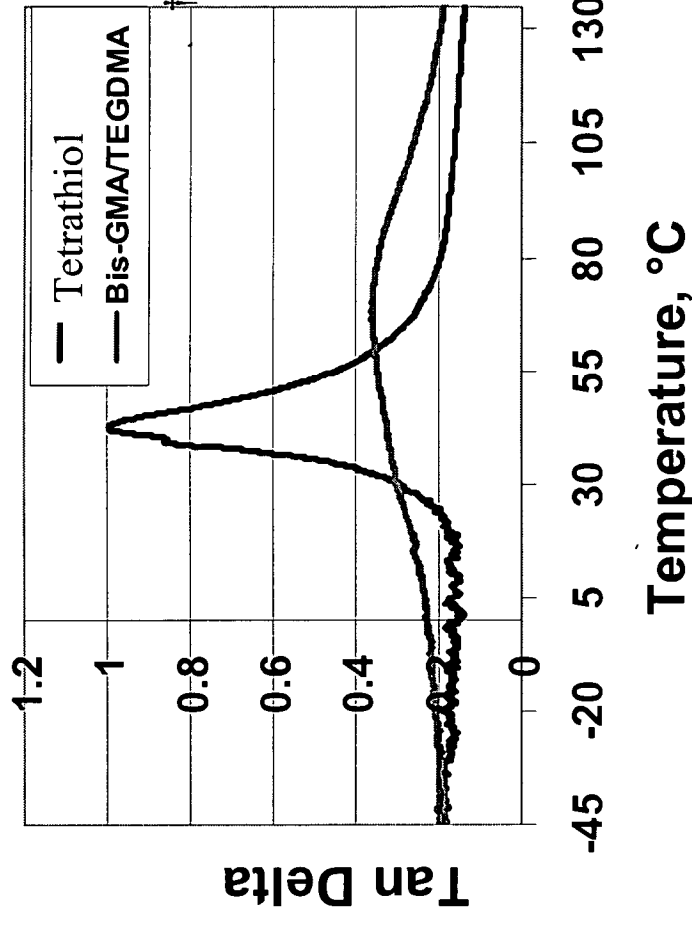
-15 -5 5 15 25 35 45 55 65 75 85 95

Temperature, °C

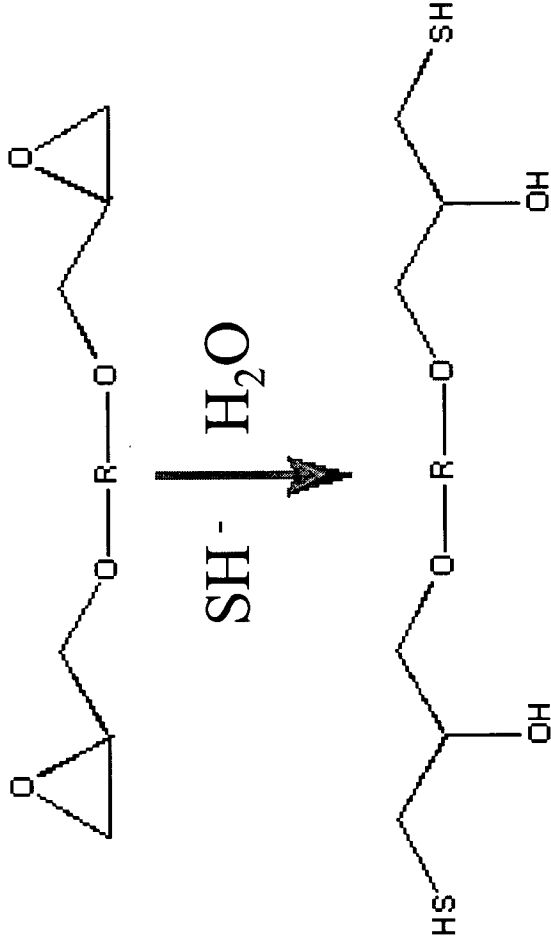
Thiol-ene systems  
show promising  
mechanical utility



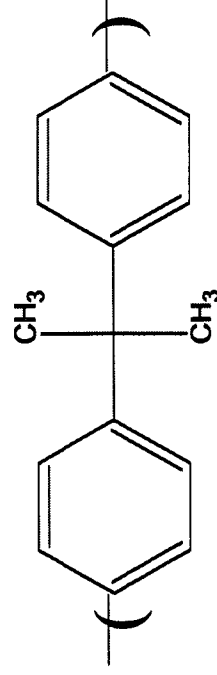
Peak Width Analysis→thiol-ene  
system is a more homogenous  
network



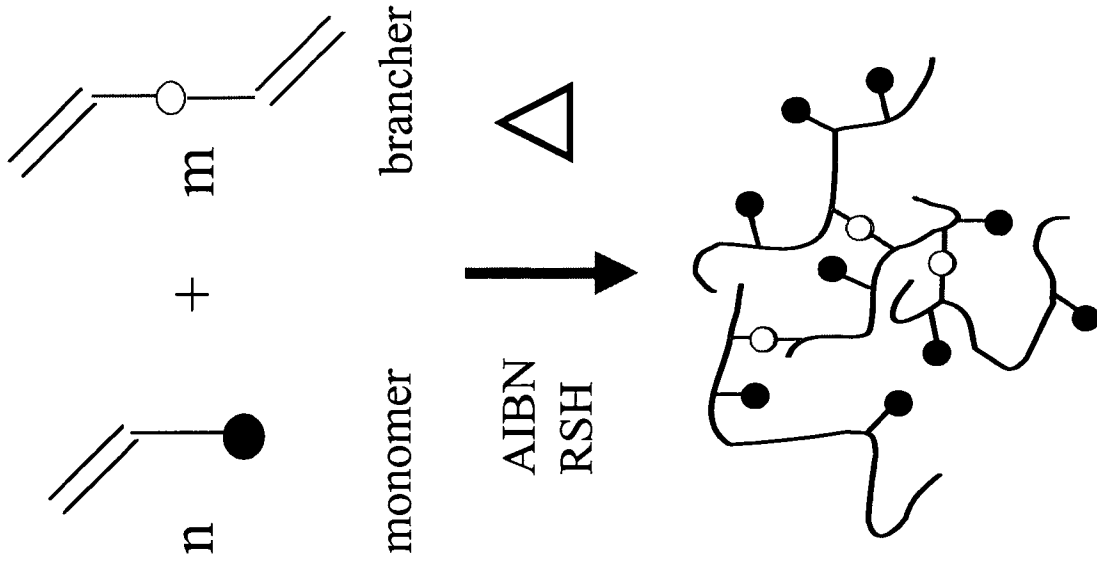
# Proposed Synthesis



where R is



Crivello, J.V. and Conlon, D.A. Aromatic Bisvinyl Ethers: *J. Polym. Sci.*, 21, 1785-1799, (1983).



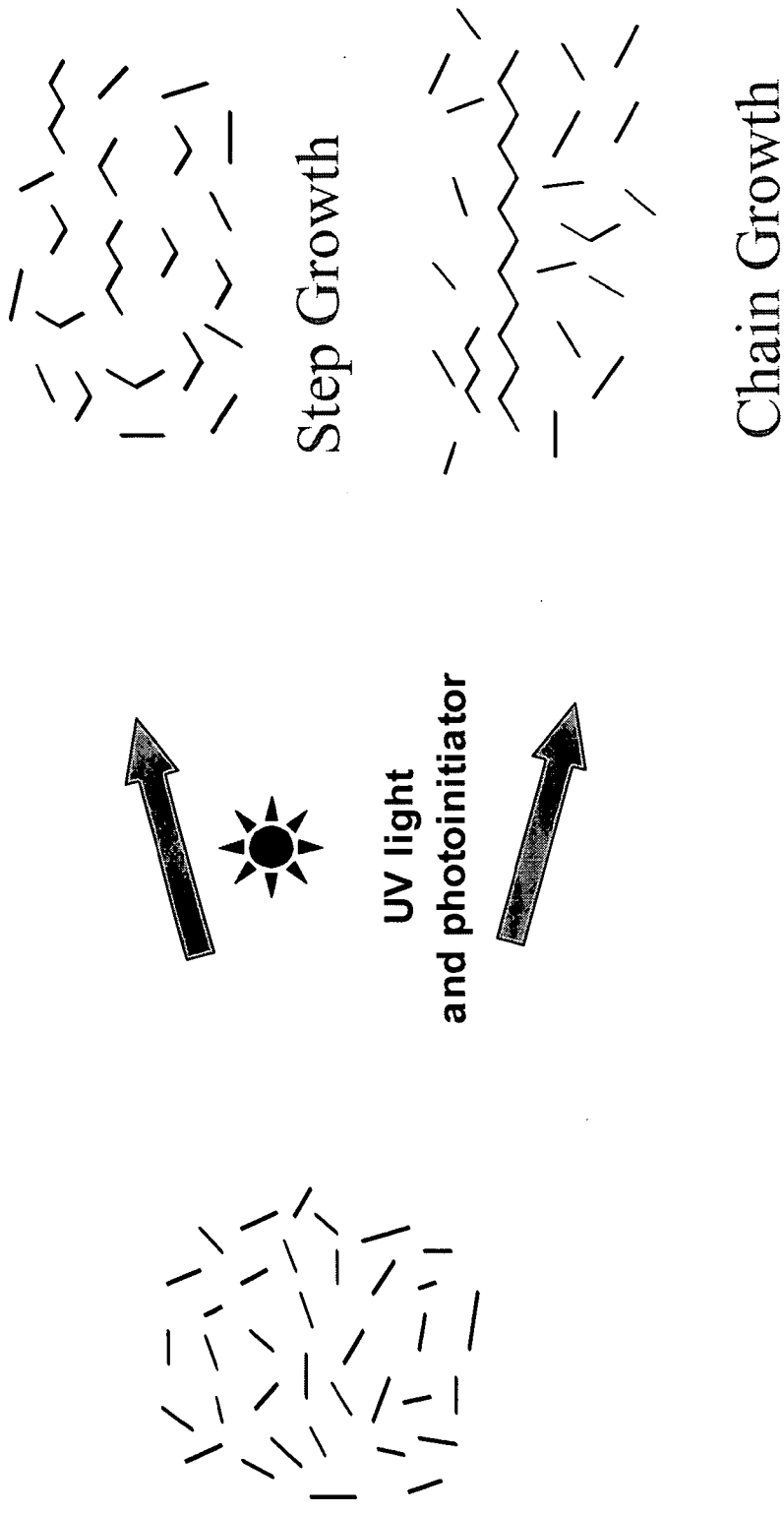
Isarure, F., Cormack, P.A.G., Sherrington, D.C... *J. Mat.. Chem.*, 13, 2701-2710, (2003).

# Conclusions

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- Thiol-ene photopolymerized systems are viable dental materials based on mechanical and kinetic evaluation
- Prepolymerization of thiol and ene monomers using photoinitiation results in lower shrinkage material
- Synthesis of novel thiol and ene monomers possessing a more rigid core show potential as dental restoration materials

# Chain Growth vs. Step-Growth

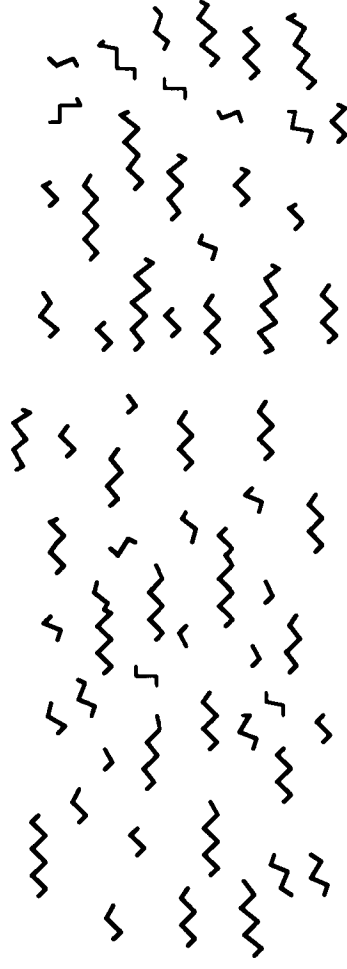


# *Delayed Gelation - Step Growth*

Propagation:  $RS\bullet + R'C=C \rightleftharpoons R'C\bullet CSR$

Chain Transfer:  $R'C\bullet CSR + RSH \rightleftharpoons RS\bullet + R'CCSR$

Step Growth



Theoretical

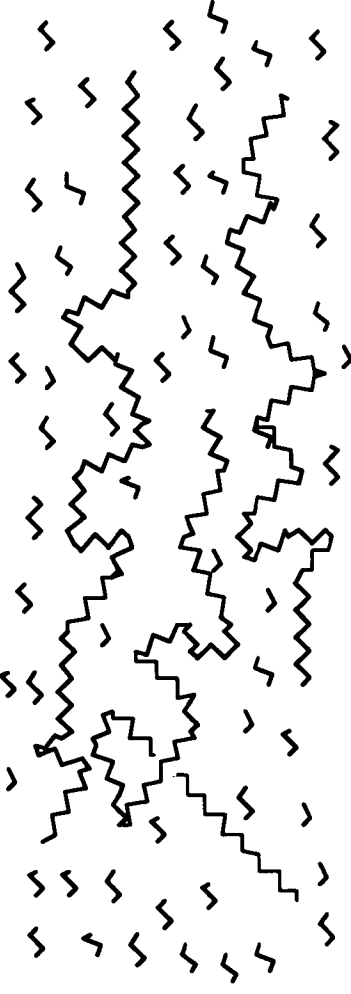
## Gel Point Conversions

tetrathiol + triallyl  
41%

trithiol + diallyl  
71%

diacrylate  
<5-10%

Chain Growth





# Thiol-Ene Conversion Results

| ene monomer         | thiol monomer | thiol conversion | ene conversion  |
|---------------------|---------------|------------------|-----------------|
| triallyl            | trithiol      | 95.2 $\pm$ 2.7   | 97.6 $\pm$ 2.9  |
| O-triallyl          | trithiol      | 87.3 $\pm$ 2.7   | 94.5 $\pm$ 1.8  |
| trivinyl            | trithiol      | 96.6 $\pm$ 1.5   | 93.8 $\pm$ 0.8  |
| O-trivinyl          | trithiol      | 95.7 $\pm$ 5.8   | 95.1 $\pm$ 4.5  |
| triazine triallyl   | trithiol      | 81.4 $\pm$ 1.6   | 95.5 $\pm$ 0.8  |
| triazine triallyl   | O-trithiol    | 86.1 $\pm$ 1.4   | 84.5 $\pm$ 2.20 |
| O-triazine triallyl | O-trithiol    | 81.3 $\pm$ 0.4   | 85.8 $\pm$ 5.6  |

# Other polymeric solutions

- Spiro orthocarbonates
  - ring opening monomers → strain-free
  - low UV stability
  - incomplete ring opening
  - Less reactive
- Fluoride releasing resin
- Cyclic ethers
  - Low shrinkage
  - good adhesion
  - Slow cure
  - Moisture uptake
  - toxicological risks

# Experimental Analysis Method

| StdOrder | Thiol  | Reaction State |
|----------|--------|----------------|
| 1        | TMPTMA | Monomer        |
| 2        | TMPTMA | Prepolymer     |
| 3        | TMPTMP | Monomer        |
| 4        | TMPTMP | Prepolymer     |
| 5        | PETMA  | Monomer        |
| 6        | PETMA  | Prepolymer     |
| 7        | PETMP  | Monomer        |
| 8        | PETMP  | Prepolymer     |

- General Factorial Design
- Two Factor Experimental Setup
  - Thiol Type: Four level
  - Reaction State: monomer vs. prepolymer
- Mechanical and kinetic experimental results weighted to create a “dental resin rating” to determine effect of factors

# Thermal Properties of Dental Restorations

- Thermal Expansion Coefficient
  - amount deformation/ thermal load
  - Enamel:  $17 \cdot 10^{-6} / ^\circ\text{C}$
  - Dentin:  $11 \cdot 10^{-6} / ^\circ\text{C}$
  - stresses  $\rightarrow$  microleakage
- Thermal diffusivity
  - Tooth:  $0.183 \text{ mm}^2/\text{s}$
  - Increased diffusivity  $\rightarrow$  increase pain sensation
- Color stability with intense light for 24h at  $37^\circ\text{C}$
- Flexural strength
  - $\geq 50 \text{ Mpa}$
  - =flexural modulus\* $0.0025+40$